

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

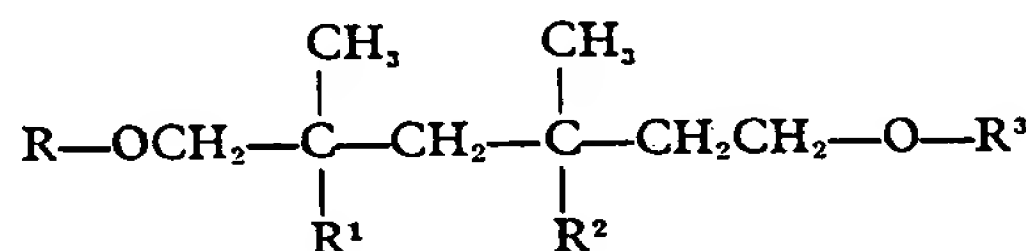
New Esters

We, W. R. GRACE & CO., a Corporation organised and existing under the laws of the State of Connecticut, United States of America, of 7, Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to

be particularly described in and by the following statement:—

THIS INVENTION relates to esters of trimethyl-1,6-hexanediol, their preparation, and polymers made therefrom.

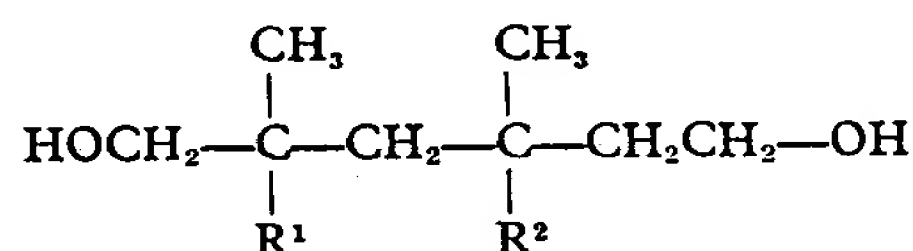
The present invention provides, as new compounds, the unsaturated esters of formula:



I

where one of R^1 and R^2 is hydrogen and the other is methyl, and one of R and R^3 is an acyl radical from an α,β -unsaturated aliphatic monocarboxylic acid preferably of 3 to 6 carbon atoms (e.g. acrylyl, methacrylyl, or crotonyl), and the other is either a saturated aliphatic acyl group of 1 to 18, preferably 2 to 6, carbon atoms or an acyl radical from an α,β -unsaturated aliphatic monocarboxylic acid, preferably of 3 to 6 carbon atoms (e.g. one of those already mentioned). These new esters are useful as monomers or co-monomers in the production of polymers containing ester groups, and as lubricating oil additives. The di-unsaturated esters of the invention are useful as cross-linking agents in free-radical-initiated vinyl polymerizations.

According to a feature of the invention, the aforesaid new esters are prepared by esterifying a trimethyl-1,6-hexanediol of formula



II

where R^1 and R^2 are as hereinbefore defined, with an acid or mixture of acids of formulae $\text{R}-\text{O}-\text{H}$ and R^3-OH , where R and R^3 are as hereinbefore defined. The acids may be used as such or as a reactive derivative thereof, e.g. a halide or lower alkyl of 1 to 4 carbon atoms ester. Preferably the diol is reacted either with the acid itself or in a transesterification reaction with a methyl or ethyl ester thereof in the presence of a strong acid catalyst, e.g. *p*-toluenesulphonic acid or sulphuric acid, with removal of the water, methanol, or ethanol (as the case may be) produced as it is formed, e.g. by azeotropic distillation. A polymerisation inhibitor, e.g.

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hydroquinone, is preferably present in the reaction mixture to prevent decomposition of the desired product.

5 This process may be carried out in one stage using two molecular proportions of the acid or derivative thereof, in which case it is especially suitable for the preparation of esters of formula I in which R and R³ are the same, though it can also be used to prepare esters in which R and R³ are different by using as starting material a 50:50 molar mixture of two appropriate acids. Alternatively the esters of formula I may be prepared in two stages from the diols of formula II by first esterifying one of the hydroxyl groups with one molecular proportion of acid for example saturated acid, to introduce one of the acyl groups R and R³ and then either esterifying the mono-ester so produced with another proportion of acid, for example unsaturated acid, so as to introduce the other acyl group, or, alternatively, by transesterifying the mono-ester with a methyl or ethyl ester of the acid, for example unsaturated acid.

25 According to a further feature of the invention, there is provided a process for the production of a polymer which comprises subjecting an unsaturated ester of formula I to the action of a free-radical-generating catalyst, e.g. α , α' -azodiisobutyronitrile or di-*t*-butyl peroxide. This polymerization may be carried out in a manner analogous to that used for the production of polymers from known unsaturated monomers using free-radical-generating catalysts. For example, the monomer and catalyst can be heated together, e.g. at 20°—100°C., in the absence of any diluent until the mixture solidifies.

40 The properties of the polymers obtained depend on whether one or both of R and R³ is unsaturated. When both are unsaturated, insoluble thermoset resins are obtained. Consequently, di-unsaturated esters of formula I are generally polymerized *in situ*. They may, for example, be used for electrical insulating purposes, e.g. as "potting" resins. On the other hand, the resins obtained by polymerization of esters of formula I in which only one of R and R³ is unsaturated are thermoplastic resins, softening at 70—120°C. and capable of being moulded in conventional injection moulding and extruding machines. They are preferably prepared by emulsion polymerization. They may be used as coatings and for impregnating textiles, for both of which purposes the resin is conveniently applied as an emulsion. Both the thermoset and thermoplastic resins are clear, water-white solids.

60 The diols of formula II may readily be prepared by hydrogenation of the corresponding trimethyl adipic acids in methanol at high temperature and pressure in the presence of a copper chromite catalyst.

65 The following Examples (in which Example

1 described the preparation of a starting material) illustrate the invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

0.5 mole (44 g.) of isobutyric acid, 96 g. (0.60 mole) of a mixture of 2,2,4- and 2,4,4-trimethyl-1,6-hexanediols, 4 g. of sulphuric acid ($d=1.84$) and 400 ml. of benzene were heated at reflux temperature with azeotropic removal of water and return of benzene. When the theoretical amount of water has been collected and water was no longer evolved, the benzene solution was washed with aqueous sodium carbonate solution several times and finally with water. The solution was dried, and the benzene distilled off under reduced pressure. The remaining viscous liquid was fractionated giving 90 g. of a mixture of 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol monoisobutyrate, b.p. 102°C./0.04 mm.Hg, $n_D^{20}=1.4460$.

The mixture of hexanediols used as starting material was prepared as follows.

A 2-litre, high-pressure autoclave was charged with 188 g. (1.0 mole) of a mixture of 2,2,4- and 2,4,4-trimethyladipic acids, 500 ml. of methanol and 25 g. of copper chromite catalyst. After flushing the autoclave with nitrogen, the gas inlet valve was connected to a hydrogen compressor and 150 atmospheres of hydrogen were pumped in. The temperature was raised to 255°C., within 40—60 minutes and the hydrogen pressure maintained at 280—300 atmospheres. After about 2—3 hours, the hydrogen absorption was complete. The catalyst was removed by filtration, and after distillation of the methanol, a crude mixture of 2,2,4- and 2,4,4-trimethyl-1,6-hexanediols is obtained as a light-yellow oil in 95—98% yield. It is a colourless liquid after redistillation, b.p. 100°C./0.05 mm. Hg., $n_D^{20}=1.4620$.

EXAMPLE 2

In a 1-litre round-bottom flask equipped with a stirrer, Dean Stark trap, reflux condenser and thermometer, were placed 1 mole (230 g.) of a mixture of 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol monoisobutyrate (prepared as described in Example 1), 1.2 moles (103 g.) of methacrylic acid, 5 ml. of sulphuric acid ($d=1.84$), 500 ml. of benzene and 0.2 g. of hydroquinone. This mixture was then refluxed for 16 hours, and 18 ml. of water were collected in the trap. The catalyst and excess methacrylic acid were removed and the crude product fractionated. 210 g. of pure mixed 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol monoisobutyrate monomethacrylate were obtained, b.p. 122°C./0.06 mm. Hg., $n_D^{20}=1.4518$, saponification equivalent=293.

EXAMPLE 3

Proceeding as in Example 2, but replacing

- methacrylic acid by crotonic acid, on distillation, 220 g. of mixed 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol monoisobutyrate monocrotonate were obtained, b.p. 125°C./0.1 mm. Hg., $n_D^{20}=1.4555$, saponification equivalent=290.

EXAMPLE 4

- In a 500 ml. round bottom flask equipped with a thermometer, a distillation column and a distillation head, were poured 46 g. (0.20 mole) of a mixture of 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol monoisobutyrate, 3 g. of *p*-toluenesulphonic acid, 6 g. of hydroquinone and 86 g. of (1 mole) of methylacrylate. A stream of nitrogen was bubbled through the reaction mixture which was heated to 100°C. The azeotropic mixture of methanol and methyl acrylate was removed as it was formed. At the end of the reaction the excess methyl acrylate and the catalyst were removed. The colourless mixed trimethyl-1,6-hexanediol monoisobutyrate monoacrylate was then distilled, b.p. 121°C./0.04 mm.Hg., $n_D^{20}=1.4539$ saponification equivalent=281.

25

EXAMPLE 5

- 40 g. (0.25 mole) of a mixture of 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol, 46 g. (0.51 mole) of methacrylic acid, 2 g. of *p*-toluenesulphonic acid, 0.5 g. of hydroquinone and 300 ml. of toluene were heated to a reaction temperature of 150°C., the water formed being removed as an azeotrope. The product was washed with aqueous sodium carbonate and finally with water. The solution was dried and the solvent removed under reduced pressure. The remaining viscous liquid was carefully distilled, giving a mixture of 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol dimethacrylates, b.p. 124°C./0.02 mm.Hg., $n_D^{20}=1.4650$. The elemental analysis of a sample and the saponification equivalent agreed with the calculated values.

EXAMPLE 6

- Proceedings as in Example 5 but replacing the methacrylic acid by crotonic acid, on distillation, a mixture of the dicrotonates was obtained as a colourless oil, b.p. 133°C./0.01 mm.Hg., $n_D^{20}=1.4699$.

EXAMPLE 7

- 20 g. of the freshly distilled mixture of monomeric trimethyl-1,6-hexanediol dimethacrylates prepared as described in Example 5, were mixed with 0.6 g. of a thickening agent (high molecular weight polymethylmethacrylate) and 0.05 g. of α,α' -azodiisobutyronitrile. The viscous mixture was placed in a water bath at 60°C. After 15 hours, the mixture had solidified to a clear, water-white, cross-linked polymer with good elastic properties, high surface hardness and good scratch resistance. The polymer was insoluble in all organic solvents and decomposed on heating about 300°C.

EXAMPLE 8

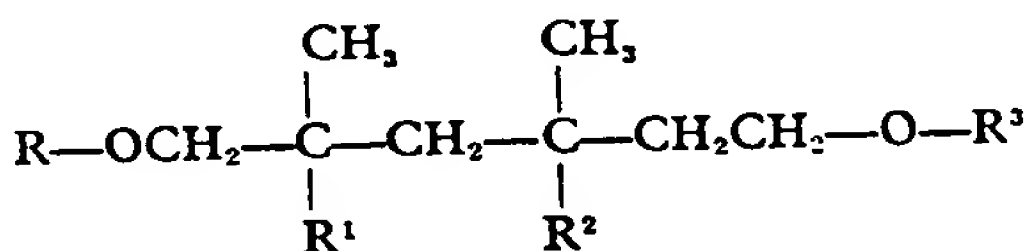
- To 30 g. of the freshly distilled mixture of trimethyl-1,6-hexanediol dimethacrylates, described in Example 5, 0.5 g. of di-*t*-butyl peroxide was added at room temperature. After 24 hours at room temperature, a solid polymer was obtained with approximately the same properties as that described in Example 7.

EXAMPLE 9

- A mixture of 30 g. of mixed 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol monoisobutyrate and methacrylate prepared as described in Example 2, 200 ml. of water, 0.75 g. of Duponol ME, 0.3 g. of ammonium persulphate and 0.23 g. of sodium bisulphate was placed in a glass autoclave fitted with a magnetic stirrer. The reaction was flushed with nitrogen and then heated to 40°C. during 24 hours with vigorous stirring. After breaking the latex by the addition of 100 ml. of concentrated sodium chloride solution, the polymer was recovered by filtration, and thoroughly washed with water. The dried polymer weighed 25 g. and had a softening point (Kofler bench) of 70—75°C. The powder could be moulded into transparent, colourless articles by conventional injection moulding.

WHAT WE CLAIM IS:—

1. Unsaturated esters of formula:



- where one of R^1 and R^2 is hydrogen and the other is methyl, and one of R and R^3 is an acyl radical from an α,β -unsaturated aliphatic monocarboxylic acid and the other is either a saturated aliphatic acyl group of

1 to 18 carbon atoms or an acyl radical from an α,β -unsaturated aliphatic monocarboxylic acid.

2. Unsaturated esters as claimed in claim 1, in which the unsaturated acyl radicals con-

tain 3 to 6 carbon atoms each, and the saturated acyl radicals (if any) contain 2 to 6 carbon atoms each.

3. 2,2,4 - Trimethyl - 1,6 - hexanediol monoisobutyrate monomethacrylate.

4. 2,4,4 - Trimethyl - 1,6 - hexanediol monoisobutyrate monomethacrylate.

5. 2,2,4 - Trimethyl - 1,6 - hexanediol monoisobutyrate monocrotonate.

6. 2,4,4 - Trimethyl - 1,6 - hexanediol monoisobutyrate monocrotonate.

7. 2,2,4 - Trimethyl - 1,6 - hexanediol monoisobutyrate monoacrylate.

8. 2,4,4 - Trimethyl - 1,6 - hexanediol monoisobutyrate monoacrylate.

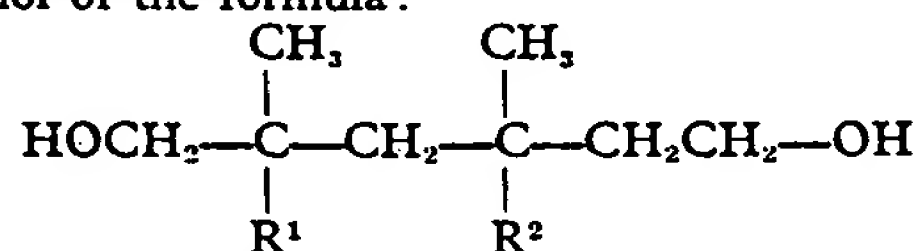
9. 2,2,4 - Trimethyl - 1,6 - hexanediol dimethacrylate.

10. 2,4,4 - Trimethyl - 1,6 - hexanediol dimethacrylate.

11. 2,2,4 - Trimethyl - 1,6 - hexanediol dicrotonate.

12. 2,4,4 - Trimethyl - 1,6 - hexanediol dicrotonate.

13. Process for the preparation of an unsaturated ester as claimed in claim 1, which comprises esterifying a trimethyl-1,6-hexanediol of the formula:



where R^1 and R^2 are as defined in claim 1, with an acid or mixture of acids of formulae $\text{R}-\text{OH}$ and R^3-OH , where R and R^3 are as defined in claim 1.

14. Process according to claim 13, in which the said diol is first esterified with one molecular proportion of a saturated aliphatic acid of 1 to 18 carbon atoms, and the mono-ester obtained is then esterified with one molecular proportion of an α,β -unsaturated aliphatic monocarboxylic acid.

15. Process according to claim 14, in which the esterification with the unsaturated acid is carried out by transesterifying the mono-ester with a methyl or ethyl ester of the unsaturated acid.

16. Process according to claim 13, in which the said diol is esterified with two molecular proportions of an α,β -unsaturated aliphatic monocarboxylic acid.

17. Process according to claim 13, substantially as described in the Examples 2 to 6.

18. Unsaturated esters as claimed in claim 1, when prepared by the process of any of claims 13 to 17.

19. Process for the production of a polymer which comprises subjecting an unsaturated ester of formula I to the action of a free-radical-generating catalyst.

20. Process according to claim 19, substantially as described.

21. Polymers produced by the process of claim 19 to 20.

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